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Effect of gas pressure on the growth of selenium thin films by pulsed laser deposition

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ABSTRACT The effect of an inert gas pressure on the structure of selenium thin films has been systematically investigated in the pulsed laser deposition process. The ablated material is deposited on Au (111) gold thin films for its characterization by atomic force microscopy (AFM). Analysis of the surface morphology shows that instead of the formation of a uniform Se thin film on top of Au (111) terraces, as it occurs in high vacuum, the film grows as two dimensional ellipsoid shaped aggregates. The size of these Se aggregates increases significantly with the gas pressure and reaches a maximum at pressures of ~ 1.5 Torr, and subsequently decreases with further increase of the gas pressure. This effect is probably due to the fact that the kinetic energy of the impinging species decreases as pressure increases, thus impeding diffusion on the substrate surface. However, further increase in the pressure prevents the Se species from being deposited on the substrate resulting in a decrease in size of the aggregates.

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1 Introduction

Laser ablation has become one of the standard methods of gas-phase cluster generation and for semiconductors and elements that easily aggregate, large clusters can be produced even in high vacuum [1]. The size of the deposited clusters can be controlled by laser parameters as power density, wavelength, and pulse duration [2]. However, the formation of large clusters during the expansion of the ablation plume requires collisions with a third body such as a background gas, in order to remove the extra energy produced by the fusion process [3]. The ambient gas conditions such as the pressure, flow rate and nature of the used gas are also parameters important for the size control [2]. The characteristics of these nanoparticles also depend on the processes occurring at the surface of the substrate, such as cluster coalescence and mobility (surface diffusion), which can be controlled by the substrate temperature [4].

Selenium, like other members of group VI elements, is characterized by its ability to form chains and rings of a variety of sizes and shapes [5, 6]. This property allows it to be efficiently confined in various zeolites and cancrinites [7, 8] forming either nanosized clusters or one-dimensional isolated chains. In bulk, it exists in several allotropic forms, from amorphous and/or vitreous to crystalline; one trigonal – a semiconductor with a band gap of 1.70 eV – and two monoclinic phases [4]. In a previous paper [9] we reported the synthesis of Se nanoparticles by laser ablation using the second harmonic of Nd:YAG laser (532 nm) and deposition on Au (111) and Si (100) substrates. In this work we investigate the influence of an inert gas pressure in the deposition system during a single pulse deposition of amorphous selenium on to gold thin films.

2 Experimental

2.1 *Laser ablation setup and sample preparation*

In these experiments we used the 532 nm second harmonic wavelength of a pulsed Nd:YAG laser with a power density of 1.35×10^8 Wcm^{-2} and a 10 ns pulse duration [9]. The laser beam was focused with a 140 mm focal length spherical lens, with incidence angle of 45°. The spot size at the surface of the target was approximately 2 mm^2. The distance between the target and the substrate was of the order of 35 mm. Commercial amorphous selenium (Baker 99.99%) was pressed at 4.8 ton cm^{-2} to make 5 mm thick and 20 mm in diameter targets. The ablated material was deposited onto gold coated glass films with atomically flat Au (111) terraces, prepared using a procedure previously published [10–12]. In all cases, the substrate was maintained at room temperature. Target and substrate were placed inside a vacuum chamber with a diffusion pump and a constant flow of Ar gas, in order to prepare different samples at pressures in the range of 50 mTorr up to 2.5 Torr. During ablation the target was rotated to avoid depletion of the material at any given spot.

2.2 *Atomic Force Microscopy (AFM) and X-Rays diffraction characterization*

For visualization of the material deposited on the different substrates we used a Nanoscope III AFM system

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(Digital Instruments, USA) operating in "tapping" mode, as has been described elsewhere [9]. All images were recorded at the very slow scan rate of 1 Hz, in order to avoid sample damaging. Due to these precautions, no impact on the tip or on the sample was observed. Images were recorded in height, amplitude and phase modes simultaneously, which allow for the measurement of the diameter and height of the deposited material. X-ray diffraction measurements were performed at room temperature in air. An angular step of 2θ of 0.04° and a fixed counting time of 10 s were taken to measure the intensity of the Bragg reflections in the range: $10° \leq 2\theta \leq 40°$.

3 Results and discussion

As explained before, gold films consisting of micron size grains with perfectly flat Au (111) terraces, were used as substrates in the present study, since nanosized features are easily recognizable on their surface. Another advantage is its relatively simple cleaning and maintenance of such substrates. These aspects make the gold film an ideal surface reference to be used for microscopy analysis. Figure 1 shows AFM image of Se deposition on the substrates at different Ar pressures: a: clean gold substrate which shows perfectly flat terraces of Au (111) located on top of micron size grains divided by deep trenches are easily seen. Selenium deposition results in changes in the surface characteristics and morphology as can be seen in Fig. 1b: 0.05 Torr; c: 1.5 Torr. At lower pressures most of the material diffuses around the grain edges of the gold substrate, where most of the aggregation process occurred, forming big chain-like structures. Few isolated aggregates appear in the top of the substrate grains. As pressure increases, more material is deposited on top of the flat grains, as can be seen in Fig. 1c. Table 1 and Fig. 2 shows the analysis of the AFM images. It reveals that the size of the aggregates reaches a maximum for a pressure of 1.5 Torr. At higher pressure the size of the aggregates diminishes, both in chains and at the top of the grain particles. Morphology revealed by AFM images indicates that material arriving to the substrate surface is more uniformly distributed. In all cases, the aggregates in top of the grain surfaces as the aggregates in the grain boundaries (chain-like structures) are formed by particles in the form of disk shaped islands.

The obtained X-ray diffractograms of the samples are presented in Fig. 3. Samples prepared at 0.05 Torr do not show any features related to any of the Se crystal phases, suggesting the amorphous nature of the deposited Se. However, for samples prepared at higher Ar pressures, two weak peaks appear

Pressure (Torr)	Se-Chains		Se-aggregates		Se-Crystal
	Width (nm)	Height (nm)	Diameter (nm)	Height (nm)	length (nm)
0.05	449 ± 93	24 ± 6	179 ± 26	10 ± 3	no
0.1	484 ± 130	24 ± 6	109 ± 18	4 ± 1.7	41.5
0.5	696 ± 168	25 ± 6	98 ± 27	4 ± 1.8	34.9
1.5	677 ± 191	35 ± 10	255 ± 73	10 ± 4.4	52.4
2.5	399 ± 99	21 ± 5	99 ± 26	7 ± 1.7	69.9

TABLE 1 Characteristics of Se particles deposited on Au (111) substrate at different Ar pressures. Data obtained by AFM image analysis and XRD diffractograms

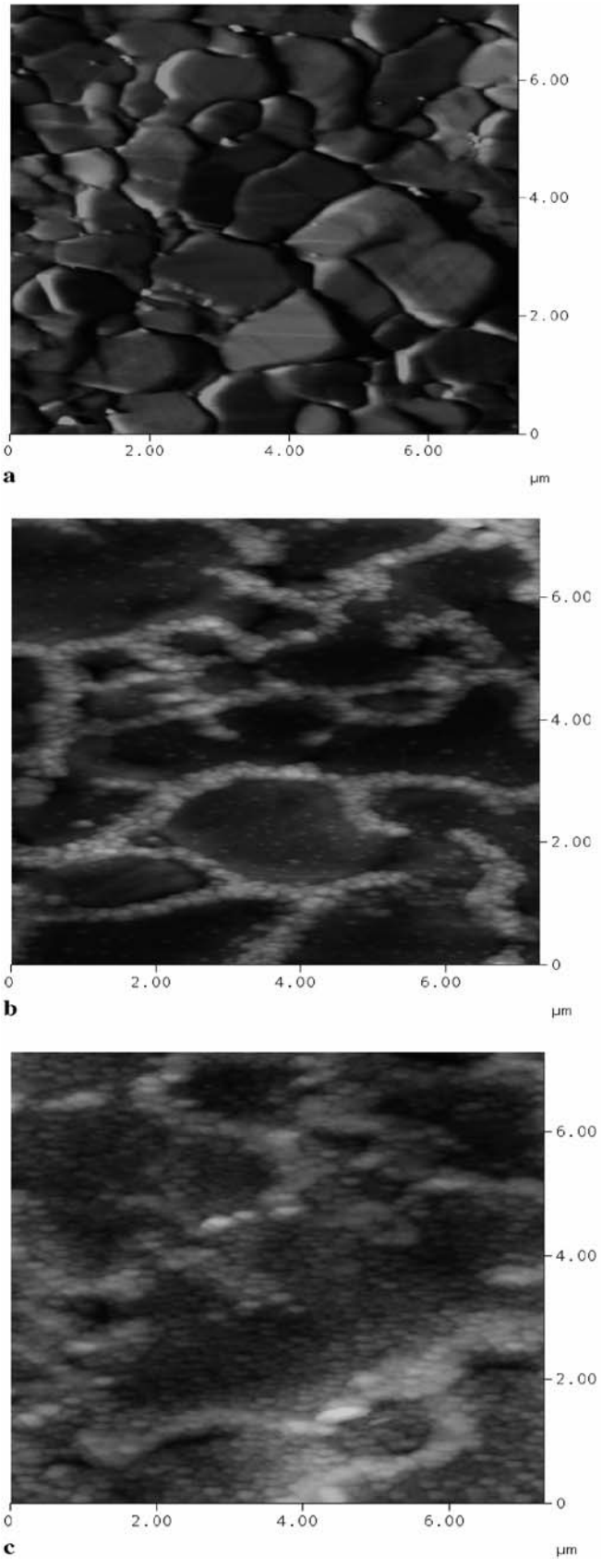

FIGURE 1 Amplitude mode AFM images of the clean gold film substrate, consisting of large grains with atomically flat Au (111) top surface (**a**); the gold film substrate covered by Se particles deposited after 1 laser pulse and at a background Ar pressure of 0.05 Torr (**b**), and 1.5 Torr (**c**) respectively. *Z* range is 0–100 nm

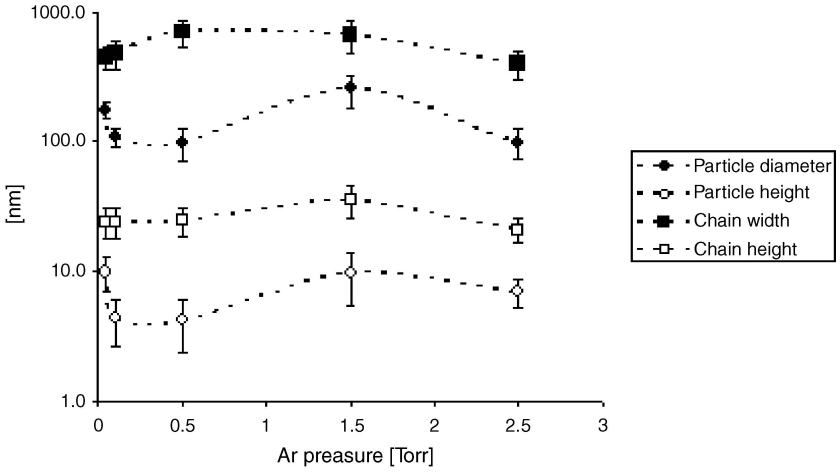

FIGURE 2 Diameter (*full circles*), height (*open circles*) of the aggregates on the top of the Au (111) grain surfaces; width (*full rectangles*) and height (*open rectangles*) of the Se particles aggregated on the gold grain boundaries as function of the background gas (Ar) pressure (1 laser pulse). Logarithmic scale on the *Y*-axis. The *dotted lines* are help for the eye

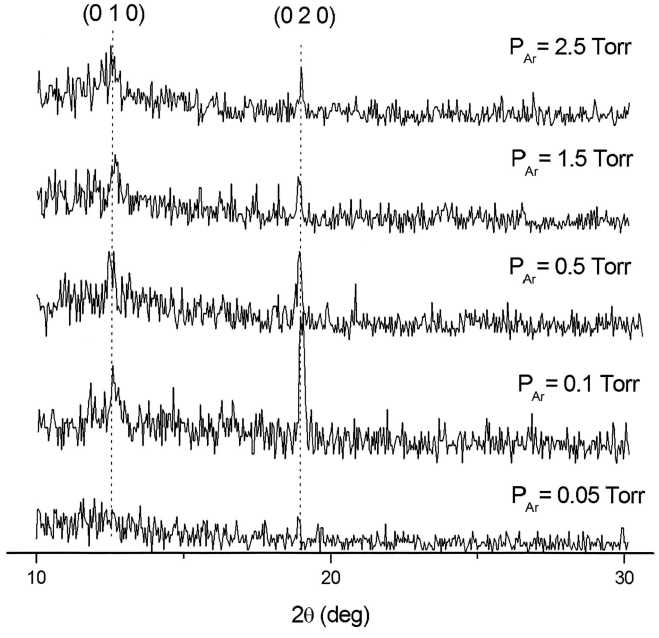

FIGURE 3 X-ray diffraction patterns of the samples. *Arrows* indicates the position of the peaks and are labelled with their correspondent Miller indexes

on the diffractograms. The comparison of the observed peaks with the standard (ICDD 24 - 1202.) shows that at least part of the deposited selenium is in the monoclinic crystal phase, mainly oriented in the (020) direction. The average crystal size was determined by the Scherrer method [13]. These results also appear in Table 1.

As can be seen from Figs. 1 and 2, the presence of a background gas results in no significant changes in the deposit for pressures between 0.05 and 0.1 Torr. Most of the deposited material goes to the grain boundaries, after particle migration along the substrate surface. For pressures higher than 0.5 Torr, the diameter of the aggregates on the grain surfaces increases, while the width of the chains decreases. At 1.5 Torr, the average size of the observed particles, both aggregates and chains, reaches a maximum. A further increase of the Ar pressure results in a more uniform distribution of the deposited material. However the size of the aggregates diminishes when compared with the samples prepared at 1.5 Torr, so it reflects a reduction of the incident particles at the substrate. The above results shows the thermalization effect of the background gas on the kinetic energy of laser ablated selenium species. In vacuum or at very low Ar pressure (0.05 Torr), clusters are generated with a large amount of internal energy. In these conditions, particles arriving at the substrate are subject to fragmentation and structural rearrangement. The presence of a background gas provides a collisional cooling that is favorable for condensation and cluster stabilization. Therefore the diffusion length of the particles arriving to the substrate is substantially reduced. XRD measurements shows structural arrangements within the deposited particles allowing crystallization. Since monoclinic Se is formed by puckered molecules of Se_8 rings [5] up to this point, it is unclear whether it is a substrate mediated phenomena or a side effect of the thermalization process induced by the background gas. However, since amorphous selenium deposition in vacuum or low Ar pressures results in amorphous selenium thin films, the present results suggests a pressure threshold for crystallinity of the deposited material.

4 Conclusions

In this work, the effects of a background gas on the synthesis of Se thin films at Au (111) surfaces is presented. The characterization of the deposited material was made by AFM and XRD. The morphology and structure of the deposited particles strongly depends on the pressure of the background gas. Indeed we found a pressure threshold for crystallinity of deposited material.

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